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INFRARED SPECTROSCOPY

JAMES R. HOUCK, BARRIE W. JONES, JUDITH L. PIPHER, BARUCH T. SOIFER

Center for Radiophysics and Space Research, Space Science Building
Cornell University, Ithaca, N. Y. 14850

Contract No. F19628-70-C-0128

Project No. 8692

Semiannual Technical Report No. 1

June 1, 1970

Contract Monitor: Stephan D. Price
Optical Physics Laboratory

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ABSTRACT

This report describes the work completed between November 15, 1969 and May 31, 1970, and is divided into four sections:

A) Detectors for the wavelength range 5μ to 30μ,

B) Detectors for the wavelength range 65μ to 1.5 mm,

C) A lamellar grating for detector calibration in the far infrared,

D) Black paint for far infrared cryogenic use.

ERRATA:

p. 3, line 17, last word should be "responsivities".
p. 3, line 19, should read "noise limited".
p. 8, line 3, eliminate the period after the first "cms".
p. 8, line 11, replace "and" with "or".
p. 8, line 13, after "10μ" insert "so radiation with $\lambda \leq 10\mu$".
p. 8, line 18, third word should be "rely".

A) Detectors for the Wavelength Range 5 to 30μ

Work on short wavelength detectors (5-30μ) has been primarily devoted to fabrication and testing of copper-doped germanium detectors, with some time spent on the testing of mercury-doped germanium detectors obtained from Santa Barbara Research Center (SBRC).

The fabrication technique used closely follows that described by T.M. Quist. [1)] Germanium blocks with evaporated copper layers were baked in an 85% argon, 15% hydrogen atmosphere at 745°C for 18 hours followed by a rapid quench. Various methods of soldering indium contacts to 3mm cubes cut from the germanium blocks were tried; no method was found to be substantially superior to any other.

The NEP's(Noise Equivalent Power) of the detectors were determined in the standard manner, using a 600°C blackbody as a reference source, and an interference filter to define the spectral response of the system (12-14 microns). All detectors were tested at 4.2°K; no attempts to test detectors at other temperatures were made. Results to date indicate the best copper doped detectors have NEP's of 5×10^{-13} watts, and responsibities of .5-1.5 amps/watt. These detectors are essentially background photon noise linited.

Mercury-doped germanium detectors supplied by SBRC were also tested to determine their NEP's. The best results to date are NEP's of $3\text{-}6 \times 10^{-11}$ watts. The copper-doped germanium detectors markedly outperform the commercially manufactured mercury-doped germanium detectors.

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1) Quist, T.M., Proc. IEEE, 56, 1212 (1968).

B) Detectors for the Wavelength Range 65μ to 1.5 mm

Work on long wavelength detectors has been primarily concerned with fabrication and testing of detectors. The spectral response and the noise-equivalent power (NEP) were measured. Filters, also necessary for the scheduled sounding rocket flight, have been constructed.

1) Gallium-Doped Germanium (Ge:Ga)

Gallium-doped germanium detectors were constructed from 3 mm cubes of gallium concentration[1] $n \sim 7 \times 10^{13}$ cm^{-3} and majority carrier mobility $\mu_{4.2^\circ K} \sim 2 \times 10^5$ cm^2 volt^{-1} sec^{-1}. After cleaning the cubes in CP-4 etch, two faces of the cube were indium soldered. Leads (copper wire) were then soldered to these two faces of the cube.

Measurements of the spectral response and NEP of the detectors were made at a detector temperature of 4.2°K. The spectral response was found by comparing the response of Ge:Ga to a golay cell using a Perkin Elmer 301 Far Infrared Spectrometer. The NEP of the detector was measured in the conventional manner using a 900°K black body. The best NEP obtained to date is 1.1×10^{-11} watts/(Hz)$^{1/2}$, a factor of fifteen higher than the background limited noise-equivalent power, NEP_{BLIP}, for the experiment. No correction for atmospheric attenuation has been made in these estimates.

For the flight, it is necessary to reject 63μ radiation from the Ge:Ga detector, because atomic oxygen in the atmosphere emits strongly at that wavelength. A Yoshinaga filter has been constructed to accomplish this rejection.

2) Gallium Arsenide (GaAs)

The gallium arsenide detector material was supplied by Professor Ballantyne of the Electrical Engineering School, Cornell University. A high-purity epitaxial layer of GaAs ($\sim 100\mu$ thick) was grown on a semi-insulating substrate. The donor concentration was $n \sim 6.4 \times 10^{14}$ cm^{-3} and the electron mobility $\mu_{300°K} \sim 7000$ cm^{2} volt^{-1} sec^{-1}.

The detectors were cut to 2 1/2 mm x 4 1/2 mm and leads were attached by two different techniques. In one method[2], small (10 mil) pellets of high purity tin were alloyed to the detector at 320°C in a hydrogen-hydrogen chloride atmosphere. Leads were then indium soldered to the tin. Professor Ballantyne also supplied one detector with gold leads that were thermal-compression bonded at 300°C and 5,000 psi to Ge-Au-Ni strips that had been evaporated and alloyed to the detector.

The NEP and spectral responses obtained for the two different detectors were identical. The NEP of the detector was $\sim 2 \times 10^{-12}$ watts/(Hz)$^{1/2}$, a factor of 6 higher than NEP_{BLIP} for the experiment. The spectral response of the detector was measured using the lamellar grating attachment to the Perkin Elmer 301 described in Section C of this report.

3) Rollin Detector (InSb)

Rollin detectors have been constructed of both high and low resistivity material. The InSb was cut to 3 mm x 5 mm x 0.3 mm and after a brief etching, leads were indium soldered to the detector.

Kinch and Rollin[3] have suggested the use of a transformer to better match the low resistivity detector to the preamplifier following it. Tests are now in progress to determine which type of Rollin detector is best for the flight system.

The spectral response of the Rollin detector has been measured with the lamellar grating, and estimates of the NEP have been made.

References

1) Moore, W.J. and Shenker, H., Infrared Physics 5, 99 (1965).

2) Stillman, G.E., Wolfe, C.M. and Dimmock, J.O., P.I.B. Intl. Symp. on Submillimeter Waves (1970)

3) Kinch, M.A. and Rollin, B.V., Brit. J. Appl. Phys. 14, 672 (1963).

C) A Lamellar Grating for Detector Calibration in the Far Infra-red

We were faced with the difficulty of calibrating far infra-red detectors using a Perkin-Elmer 301 spectrophotometer with a diffraction grating (d.g.). The main problem is that the flux from the source (a high pressure mercury arc) falls off rapidly at long wavelengths resulting in a very small usable flux after the d.g. monochromator. The advantages of a lamellar grating (l.g.) in the far infra-red are well known[1,2,3,4] hence it was decided to replace the d.g. with a l.g. for measurement in the submillimeter region. The l.g. module has proven to be an inexpensive unit which was also easy to construct, and which is easy to install, align and use. It can be used with far infra-red spectrometers other than just the P.E. 301, provided that they are grating instruments that employ the Littrow entry/exit slit mode.

Our l.g. operates over a wave number κ range, $3\text{cm}^{-1} \leq \kappa \leq 200\text{cm}^{-1}$ (wavelength λ, $50\mu \leq \lambda \leq 3\text{mm}$) with a maximum resolution of 0.2 cm^{-1}. This is significantly better than the 1 cm^{-1} d.g. resolution. At 20 cm^{-1} it achieves a signal-to noise ratio about 200x that of the d.g. Fig. 1 shows some spectra obtained with both fairly dry nitrogen and water vapor saturated nitrogen in the P.E. 301.

The size of the l.g. is 6.5 x 6.0 cms. and was dictated by the beam size at the d.g. mounting position. An excursion of 2.5 cms was adopted,

because this determines the resolution, the resulting resolution being sufficient for our purposes, and because the l.g. could then be built around a standard 1" micrometer thread. Each tine is 0.5 cms. wide giving a period of 1.0 cms.

The long wavelength limit is determined by a cavity effect caused by the l.g. profile. Milward[3)] shows that in the case of a grating of period 1 cm which receives unpolarized radiation this cavity effect limits the resolution at 3 cm^{-1} to 0.1 cm^{-1}. Hence the excursion determined resolution of 0.2 cm^{-1} is degraded only at wave numbers smaller than $\sim$ 3 cm^{-1}. The period chosen enables us to operate at the longest infra-red wavelengths.

The short wavelength limit may be determined by either the optical finish of the l.g. surfaces and the accuracy with which the two sets of tines can be aligned with respect to each other. The ground finish of the tines is of size $\sim$ 10μ is strongly scattered. This is a desirable feature which tends to remove short wavelength radiation, which is unwanted since it causes a reduction in interferogram fringe contrast. It also necessitates use of a very small increment in l.g. excursion in order that the short wavelength spectra are not injected as noise at longer wavelengths. (However, we relay mainly on filters elsewhere in the system to reduce unwanted radiation.) The two sets of tines are flat to $\sim$ 10μ and can be made parallel to $\sim$ ±1' of arc. Thus the maximum spurious path difference between the extremities of the grating due to this non-parallelism is $\sim$ 30μ, which only results in serious attenuation ($< 2/\pi$) of usable flux at wavelengths < 60μ (170 cm^{-1}).

The widths of the entry and exit slits also affect the short wavelength limit. One effect of the entry slit is known as Jacquinot's limit[2] and is not a limiting effect here. However, a combined effect of the entry and exit slits is more serious and the entry/exit slit has to be narrowed to avoid the reduction of interferogram fringe contrast which would arise from the collection of higher orders [4]. Such a reduction of slit width <u>does</u> result in a net increase of effective flux at shorter wavelengths. In our case using the full slit width only optimizes the flux at wavelengths > 200μ approximately.

The excursion can be done continuously or incrementally. We have adopted the latter mode. The increment, Δ, in separation of the two sets of tines, at which measurements are taken, determines the maximum resolved wave number k_{max} by means of the criterion

$$k_{max} \sim 1/4\Delta \quad .$$

We chose a minimum Δ of 0.0005" which corresponds to $k_{max} \sim 200 \text{ cm}^{-1}$ (wavelength ∼ 50μ). This value of k_{max} is consistent with the constraints discussed above.

For the time being the excursion is accomplished by direct drive by hand. The increments are determined by means of a disc with grooves across the circumference that locate on a spring loaded ball. Automation is planned and will be based on a stepping motor and a level detector, the latter in order to exclude readings during which noise spikes occur in excess of some threshold.

In each position the signal is integrated over time. The source is chopped at 13 Hz and the output from the Golay cell detector is passed through a phase sensitive detector (p.s.d.).

The d.c. output of the p.s.d. is proportionally converted to a frequency which is counted (integrated) for a preselected length of time. The spectra are derived from the interferograms by means of the Cooley-Tukey fast Fourier transform algorithm[6].

To limit the spectral range admitted to the l.g., only transmission filters are used, the rest of the optics being specular (with the exception of the ground tines). These filters are made from various combinations of black polyethylene, fused silica and Yoshinaga filters[5].

Fig. 1 shows spectra obtained with a mercury source, a filter of black polyethylene and a Yoshinaga filter of powdered NaCl, NaF, MgO in the ratios 2:1:1 embedded in "clear" polyethylene. This filter system was designed to admit wavelengths > 100μ.

Curves 1 and 2 show unapodized and apodized spectra when the whole P.E. 301 system was filled with nitrogen at 25°C which was near saturation with water vapor giving ∿ 25 Torr of water vapor over a path length of about 2.7 m. Note that the saturated absorption lines were not resolved sufficiently to maintain the saturated appearance in the reduced resolution apodized case. The positions of the absorption lines agree well with other data.[1]

Curves 3 and 4 in Fig. 1 show spectra obtained after several hours of purging with dry nitrogen. Purging was considered complete when the output signal attained a constant value.

We conclude from these results that purging can be sufficently well accomplished to permit use of the l.g. over the whole wavelength range with

a resolution of $\sim 0.5\ cm^{-1}$ and over portions of the range where water vapor does not absorb with the maximum resolution, namely $0.2\ cm^{-1}$.

The l.g. has already been used to calibrate many detectors including Rollin detectors and gallium arsenide detectors and features in responsivity occur in these in accord with other people's results.

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6) J.W. Cooley, J.W. Tukey, Math. of Comput. 19, 297 (1965).

FIGURE CAPTION

Fig. 1 Far infra-red spectra from a Perkin Elmer 301 with a lamellar grating.

Curve 1, Unapodized spectrum showing "lines" largely due to 25 Torr of water vapor, path length 2.7 m.

Curve 2, Apodized version of curve 1 using triangular apodizing function.

Curve 3, Unapodized spectrum with a "dry" nitrogen filled spectrometer.

Curve 4, Apodized version of 3, as before.

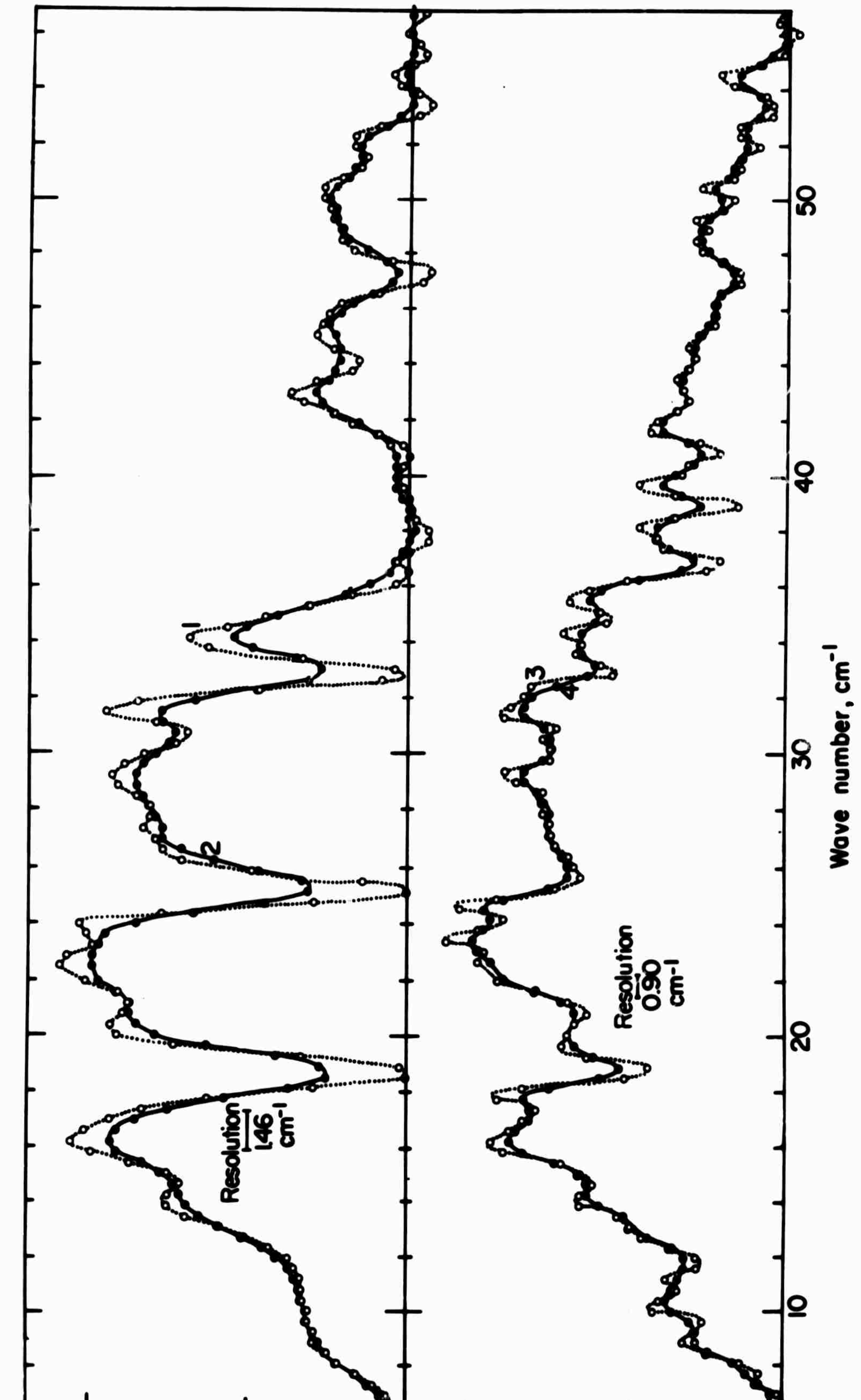
Spectral intensity, arbitrary units per cm^{-1}
Wave number, cm^{-1}
Resolution 1.46 cm^{-1}
Resolution 0.90 cm^{-1}
0
50
100
10
20
30
40
50
1
2
3
4

Figure 1.

D) Black Paint for Far Infrared Cryogenic Use

A convenient 'black paint' has been developed that remains absorptive even at long wavelengths. This paint has excellent surface stability at liquid helium temperature and is resistant to abrasion and flaking.

Microwave absorbers are often constructed of dielectrically lossy pyramids arrayed on a substrate with the tips pointing away from the substrate.[1)] The tapered structure matches the impedance of free space to the absorbing bulk. The 'paint' is similar in concept to the microwave absorber. The surface is prepared in the following manner. A commercial black undercoat is sprayed on a clean metallic surface. A hairy flock is subsequently dusted on the surface while it is still tacky. A thin coat of optical black paint, sprayed on top of the flocked surface, completes the 'black paint'.

An integrating sphere has been constructed, operable at 4.2°K and at long wavelengths. Previously, a long wavelength integrating sphere had been developed[2)], but it was not suitable for cryogenic environment. Using the sphere, the diffuse reflectance of the 'paint' was measured at various wavelengths in the 60-130μ range. Additional measurements were made at wavelengths out to 1 mm in a flight-telescope black body test. All measurements indicate that the paint is highly absorptive, even at long wavelengths.

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1) Dielectric Materials and Applications, ed. Von Hippel (MIT).

2) Morris, J.C., Applied Optics 5, 1035 (1966).

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13. ABSTRACT

This report describes work completed between Nov. 15, 1969 and May 31, 1970, and is divided into four sections:
A) Detectors for the wavelength range 5μ to 30μ;
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